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(54) X-ray windows.

(57) An X-ray window comprising a membrane of diamond one surface of which has formed upon it an array of diamond ribs so as to provide an integral supporting structure. Methods of manufacturing also are described.

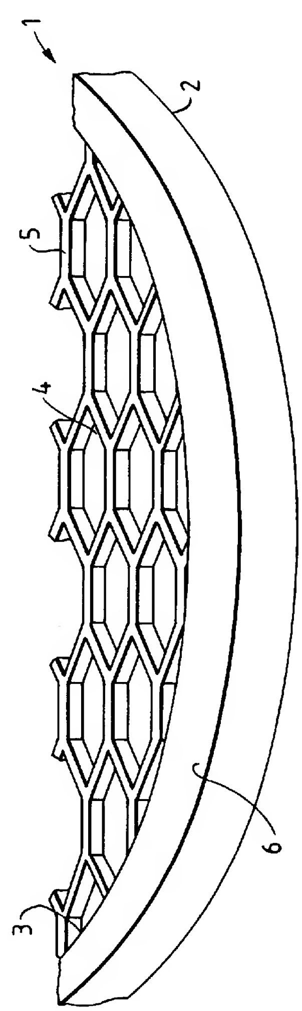

Fig. 1

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The present invention relates to X-ray windows and more specifically, to such windows made out of diamond.

X-ray windows as their name implies are thin, that is to say less than 10 μm, more specifically less than 1 μm, lamina which are transparent to X-rays and form part of X-ray apparatus. Often, as for example in connection with X-ray spectrometers, they need to be able to withstand pressure differentials of an atmosphere or greater. A material which is particularly suitable for use as an X-ray window is diamond. However, in thin lamina form it is weak mechanically and needs to be supported on a substrate. Existing practice is to grow the diamond from the vapour phase upon a relatively thick silicon substrate. Unfortunately, silicon is a relatively heavy absorber of X-rays so that diamond on silicon X-ray windows have low X-ray transmissions.

It is an object of the present invention to provide an improved diamond X-ray window.

According to the invention in one aspect there is provided an X-ray window comprising a membrane of diamond one surface of which has formed upon it an array of diamond ribs so as to provide an integral supporting structure.

According to the invention in another aspect there is provided a method for the manufacture of an X-ray window comprising the operations of depositing a layer of diamond upon a substrate material, forming an array of ribs upon the exposed surface of the layer of diamond and removing the substrate material to provide a membrane of diamond having an array of integral supporting ribs formed upon one surface thereof.

The array of ribs may be formed by removing diamond from selected areas of the exposed surface of the layer of diamond or by further depositing diamond upon selected areas of the exposed surface of the layer of diamond.

Diamond may be removed from the selected areas of the exposed surface of the layer of diamond by a chemical etching process, ion beam thinning or by ablation. In the latter case, the ablation can be carried out by means of a laser which produces radiation having wavelengths in the regions of 190 to 250 nm, where diamond absorbs strongly.

Preferably the substrate is made of silicon.

It is to be understood that for the purposes of the present application, the word diamond includes the material known as diamond-like carbon which has many of the properties of diamond but does not have the regular crystalline structure of diamond.

The invention will now be described, by way of example, with reference to the accompanying drawings in which

Figure 1 shows a three-dimensional view of a portion of an X-ray window embodying the invention, and

Figure 2 is a flowsheet of a process for producing a diamond window embodying the invention, and

Figure 3 is a flow sheet of a second process for producing a diamond window embodying the invention.

Referring to Figure 1 of the drawings, an X-ray window embodying the invention consists of a circular membrane 1 made of diamond. The membrane 1 has a plane surface 2 and a second surface 3 in which is formed an array of hexagonal depressions 4. The lands between the depressions 4 form a series of ribs 5 between the depressions 4. The result is to provide a relatively thin membrane which is integral with an array of supporting ribs. To facilitate the mounting of the X-ray window, an annulus 6 is left around the edges of the membrane 1.

The depressions may have shapes other than hexagonal, for example, they may be square-shape.

Referring to Figure 2, a process for producing an X-ray window such as that shown in Figure 1 includes the operations of

1) forming an oxide layer on the rear surface of a silicon wafer such as those used in the production of microelectronic devices.

2) Removing selectively the oxide layer from one plane surface of the wafer to form an annulus.

3) Preparing the exposed silicon surface of the wafer to provide nucleation sites for the growth of a layer of diamond upon that surface. This may be done by mechanical or ultrasonic abrasion of the exposed surface of the wafer using < 1 μm diamond grit.

4) Cleaning the prepared surface of the silicon wafer using methods which are well-known in the semiconductor art.

5) So placing the silicon wafer in a deposition chamber that the prepared surface will be exposed to the action of a gaseous reactive medium consisting of a mixture of hydrogen and methane.

6) Evacuating the reaction chamber to a pressure of about 10^{-6} torr, admitting a mixture of hydrogen and methane to the chamber, the methane concentration being in the range 0.5 to 1.5% by volume flow rate, establishing a plasma in the reactive medium by means of microwave radiation, a frequency of 2.45 GHz being satisfactory, maintaining a total gas pressure in the reaction chamber in the range 20 to 50 mbar, and allowing the reaction to proceed until a layer of diamond typically 10 μm thick has been formed on the exposed surface of the silicon wafer. During the deposition process, the temperature of the wafer is kept at a constant temperature between 850 and 900°C, although temperatures between 500 and 950°C can be used.

7) The wafer is removed from the reaction chamber, and using standard photolithographical techniques, an annulus of silicon oxide-nitride is pro-

duced around the edge of the silicon wafer.

8) The wafer and diamond coating are clamped to a support and the surface of the diamond layer is exposed to laser radiation through a transfer mask having an array of holes corresponding to the array of depressions 4 to be formed in the diamond membrane. The laser radiation has a frequency such as to be absorbed by the diamond, with a consequent graphitisation/ablation of the diamond. The etching of the diamond is continued until the thickness of the layer of diamond is reduced to about 1 μm. ArF (193 μm) or KrF (248 μm) are suitable lasers for the etching process.

9) The silicon wafer is then removed from the diamond membrane by means of standard chemical etching techniques.

In an alternative process which is illustrated in Figure 3 but which is not described in detail, after an initial diamond deposition stage, which can be the same as stages 11 to 6 of the process described with reference to Figure 1, a patterned mask of SiO_xN_y is deposited or formed on the exposed surface of the diamond layer and the diamond layer is subjected to a further diamond deposition process to build up the array of supporting ribs 5. The mask is then removed by a chemical etching process. The final stage of the manufacturing process is as before.

Claims

1. An X-ray window wherein there is provided a membrane (1) of diamond one surface (3) of which has formed upon it an array of diamond ribs (5) so as to provide an integral supporting structure.

2. An X-ray window according to Claim 1 wherein the thickness of the membrane (1) between the supporting ribs (5) is about 1 μm and the ribs (5) have a thickness of about 10 μm.

3. A method for the manufacture of an X-ray window wherein there is included the operations of depositing a layer (1) of diamond upon a substrate material, forming an array of ribs (5) upon the exposed surface (3) of the layer (1) of diamond and removing the substrate material to provide a membrane (1) of diamond having an array of integral supporting ribs (5) formed upon one surface (3) thereof.

4. A method according to Claim 3 wherein there is included the operation of removing material from selected regions (4) of the exposed surface (3) of the layer (1) of diamond thereby to provide the array of ribs (5) providing the integral supporting structure.

5. A method according to Claim 4 wherein there is included the operations of interposing a protective mask between the exposed surface (3) of the diamond layer (1) and a source of intense radiation, the mask being adapted to delineate those regions (4) of the diamond layer (1) from which material is to be removed, and subjecting the diamond layer (1) to the said radiation until the thickness of the diamond layer (1) in the said regions (4) is reduced to a pre-determined value.

6. A method according to Claim 5 wherein the intense radiation is laser radiation.

7. A method according to Claim 6 wherein the laser radiation is produced by an argon fluoride or a krypton fluoride laser.

8. A method according to Claim 4 wherein there is included the operations of forming by photolithography a protective mask on the exposed surface (3) of the diamond layer (1), the protective mask being adapted to delineate those regions (4) of the diamond layer from which material is to be removed and contacting the exposed regions (4) of the surface (3) of the diamond layer (1) with a chemical etchant until the exposed regions of the surface of the diamond layer have been reduced to a predetermined value.

9. A method according to Claim 3 wherein there is included the operations of initially forming a layer (1) of diamond of uniform predetermined thickness over the surface of the substrate, forming a protective mask on the surface (3) of the initial layer (1) of diamond, the mask being adapted to delineate those regions of the diamond layer where the array of integral supporting ribs (5) are to be formed, continuing the deposition of the diamond until supporting ribs (5) of a desired thickness have been formed on the diamond layer (1), and removing the protective mask.

10. A method according to any preceding claim wherein the diamond is deposited by preparing a surface of the substrate to provide nucleation sites to facilitate the growth of diamond upon the said surface of the substrate, placing the substrate in a reaction chamber, evacuating the reaction chamber, admitting a mixture of hydrogen and methane to the reaction chamber, the methane concentration in the hydrogen being in the range 0.5 to 1.5 $^{v}/_{o}$ by flow rate, establishing a plasma in the mixture of hydrogen and methane in the reaction chamber, maintaining a total gas pressure in the reaction chamber in the range of 20 to 50 mbar, maintaining the temperature of the substrate at a constant temperature within the

range 500 to 900°C and terminating the reaction when a pre-determined thickness of diamond has been deposited.

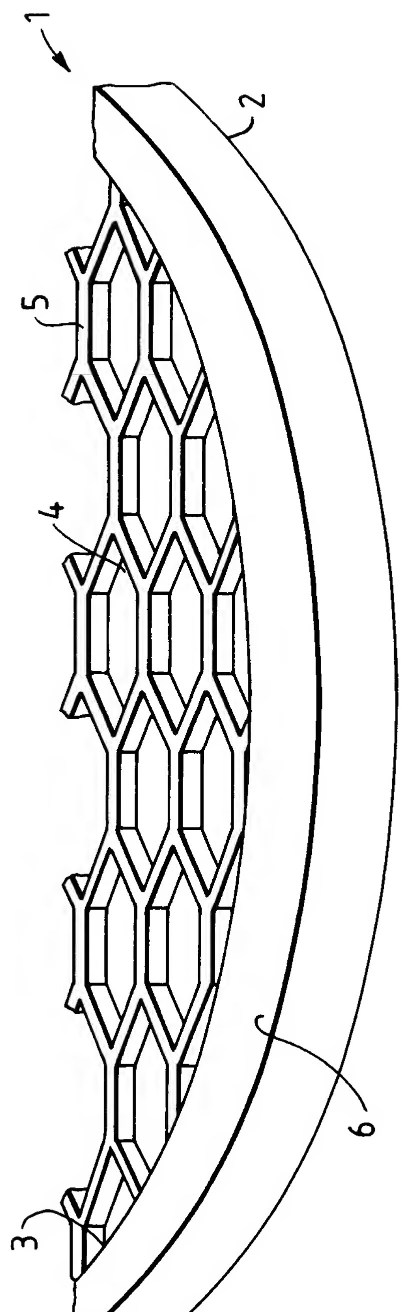


Fig. 1

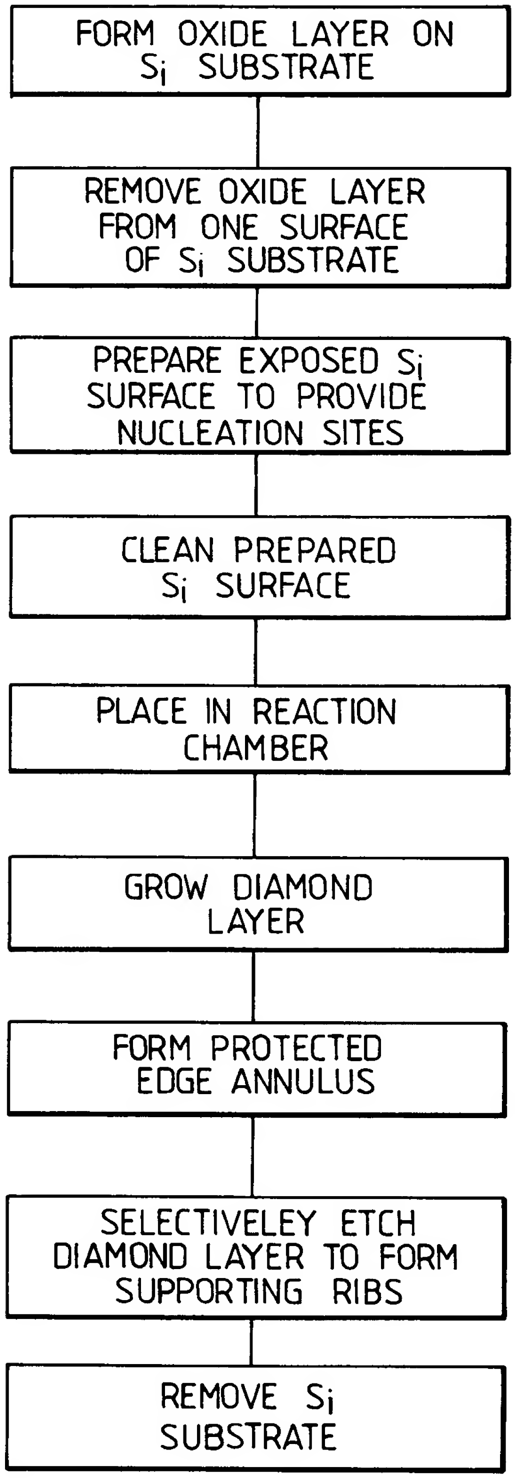
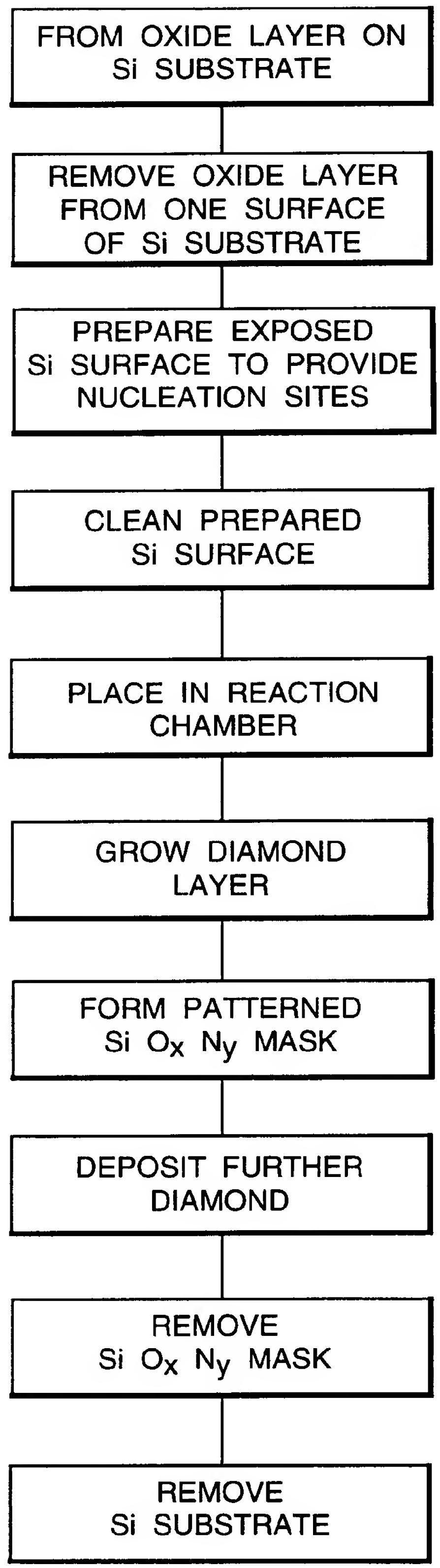

FORM OXIDE LAYER ON S_i SUBSTRATE
REMOVE OXIDE LAYER FROM ONE SURFACE OF S_i SUBSTRATE
PREPARE EXPOSED S_i SURFACE TO PROVIDE NUCLEATION SITES
CLEAN PREPARED S_i SURFACE
PLACE IN REACTION CHAMBER
GROW DIAMOND LAYER
FORM PROTECTED EDGE ANNULUS
SELECTIVELEY ETCH DIAMOND LAYER TO FORM SUPPORTING RIBS
REMOVE S_i SUBSTRATE

Fig. 2

Fig.3.


FROM OXIDE LAYER ON Si SUBSTRATE
REMOVE OXIDE LAYER FROM ONE SURFACE OF Si SUBSTRATE
PREPARE EXPOSED Si SURFACE TO PROVIDE NUCLEATION SITES
CLEAN PREPARED Si SURFACE
PLACE IN REACTION CHAMBER
GROW DIAMOND LAYER
FORM PATTERNED $Si\ O_x\ N_y$ MASK
DEPOSIT FURTHER DIAMOND
REMOVE $Si\ O_x\ N_y$ MASK
REMOVE Si SUBSTRATE

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 1965

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	EP,A,0 476 827 (SUMITOMO ELECTRIC INDUSTRIES) 25 March 1992 * column 3, line 54 - line 57 * * column 4, line 16 - line 56 * * column 6, line 18 - column 7, line 49 * * column 8, line 37 - line 46 * * claims 1,5 * ---	1-3,9 5,8,10	G21K1/10 H01J35/18
A	WO,A,93 00685 (MUELLER MARGHERITA T & LF ;GARG DIWAKAR (US); MONK VYRIL A (US)) 7 January 1993 * page 8, line 20 - page 9, line 14 * * page 10, line 14 - line 29 * ---	2,10	
A	DATABASE INSPEC INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 4858883, RAVET M F ET AL 'Realization of x-ray lithography masks based on diamond membranes' * the whole document * & MATERIALS ASPECTS OF X-RAY LITHOGRAPHY. SYMPOSIUM, MATERIALS ASPECTS OF X-RAY LITHOGRAPHY. SYMPOSIUM, SAN FRANCISCO, CA, USA, 12-14 APRIL 1993, 1993, PITTSBURGH, PA, USA, MATER. RES. SCO, USA, pages 103-109, ---	10	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G21K H01J
A	US,A,5 039 203 (NISHIKAWA AKIRA) 13 August 1991 -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	7 July 1995	Capostagno, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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